

WorléePur Si

Properties of silane-functional polyurethane-urea binders compared to classic two-component polyurethane coatings.



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Introduction

The discovery of polyurethanes in the 1930s by a group of researchers led by Otto Bayer not only changed the coatings industry for good.

The urethane group [Fig.1] characterizes all polyurethanes, such as polyurethane dispersions, two-component polyurethane coatings, urethanized alkyd resins or moisture-curing prepolymers.

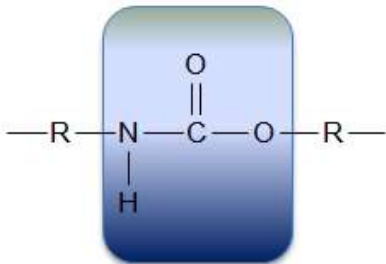


Figure 1: Urethane group

This group determines a significant proportion of the properties of the binder or coating systems in which they are contained. The properties include, for example, chemical resistance, weather resistance, abrasion or adhesion properties. Based on the polyol used, soft and flexible, tough elastic or hard coating films are obtained.

Since the discovery of polyurethanes, a wide variety of systems have been developed, particularly in the field of coating materials. Even today, polyurethane

technology represents the state of the art and is mostly used in coating systems to which high standards are applied.

Classic two-component polyurethane coatings

Chemical structure

Various hydroxyl-bearing polyols are used in the formulation of classic two-component polyurethane coatings. These usually form the binder base in what is known as component A. Depending on the later desired properties, a variety of polyols such as polyacrylates [Fig. 2], polyesters [Fig. 3], polyethers, polycarbonate diols [Fig. 4] and others can be used alone or in combination.

For example, polyacrylates usually result in faster drying and higher hardness than polyesters. On the other hand, they usually have better mechanical properties such as better flexibility.

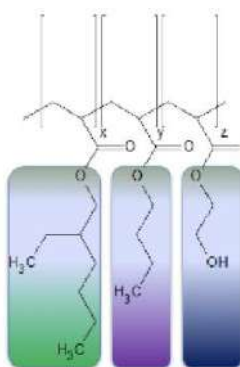


Figure 2:
 Polyacrylate

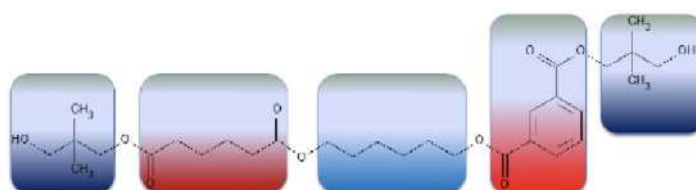


Figure 3: Polyester

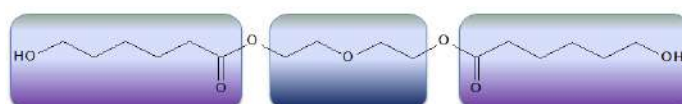


Figure 4: Polycarbonate diol

In combination with the coating isocyanate [Fig. 5], the polyols can crosslink and form the urethane group. This coating isocyanate is mostly used in the so-called component B.

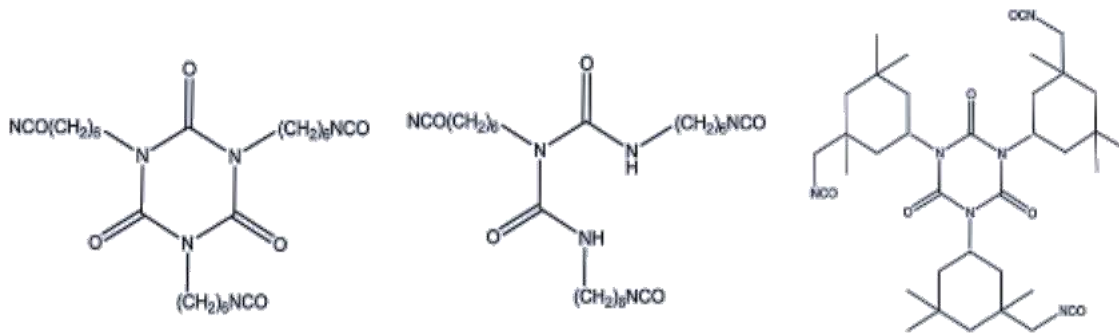


Figure 5: Paint isocyanates - HDI Trimer, HDI Biuret and IPDI Trimer

Networking basics

Before the coating materials are applied, the polyol-containing component A is mixed with the coating isocyanate-containing component B and the reaction of the hydroxyl groups of the polyols with the isocyanate groups of the coating isocyanates can start. This is an addition reaction [Fig. 6]. This reaction takes place within a certain period of time and usually cannot be stopped.

During the reaction, a three-dimensional network forms as the coating viscosity increases. At a certain point, the viscosity is too high to continue processing the coating. This time is called pot life or processing time.

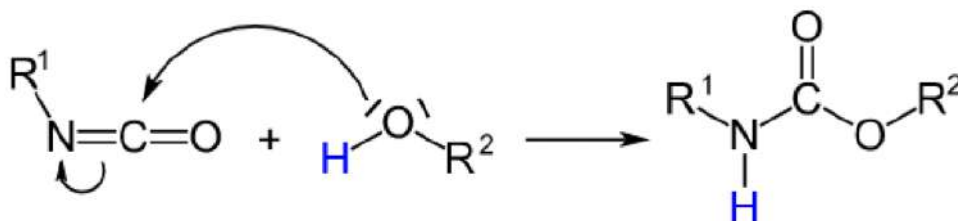


Figure 6: Addition reaction between isocyanate and hydroxyl group

High Solid vs. conventional systems

In the course of time, it has become necessary to reduce the content of organic solvents in two-component polyurethane coatings. Reasons for this are, for example, better environmental compatibility or better health protection.

To achieve this, it is necessary to increase the non-volatile content of the coating systems, which is achieved by using high-solids coating isocyanates and also binders. Compared to conventional products, the high-solids binders must have a higher non-volatile content while still maintaining a similar viscosity. This can be achieved by lowering the average molar mass and at the same time aiming for a narrower molar mass distribution. However, when crosslinking these products with paint isocyanates, this leads to a slower build-up of the molecular weight and, accordingly, to slower

drying. At the end of drying, the high solid must also be very well crosslinked and smaller molecular chains simply need longer for this.

For clarification, one can compare corresponding products. Table 1 shows the comparison of a conventional with a high solid acrylate. Both products have a comparable content of hydroxyl groups, so will also achieve comparable resistance properties in the fully cured film.

The high solid product shows a significantly higher non-volatile content of 75% compared to 60%. The viscosities are comparable for the respective non-volatile fractions.

	Conventional acrylate	High Solid acrylate
Non-volatile content	60%	75%
Viscosity	3,500 - 5,000 m-Pas	5,000 - 10,000 m-Pas
OH content on solid binder	4.5%	4.5%

Table 1: Comparison polyacrylates - conventional vs. high solid

The use of such high solid polyacrylates in corresponding coating systems leads to significantly higher non-volatile contents and reduced contents of volatile organic compounds. To illustrate this, one can look at the effect of using both products in comparable coating systems. For this purpose, both binders were used for the formulation of a clearcoat and adjusted to the same processing viscosity. In Table 2, it is easy to see that the coating based on high solid polyacrylate has a non-volatile content that is about ten percent higher in the ready-to-use state. As a result, the proportion of volatile organic compounds drops by more than 100 grams per liter of coating.

Considering only these properties and the cured paint surface, at least the formulation of such low-solvent paints is quite possible.

On the other hand, it is also important for the processor that the coatings to be applied dry sufficiently quickly in order to avoid excessively long service lives. And it is precisely here that great differences in the use of binders become apparent.

Already during the drying process (dust-dry), large differences can be observed in Table 2. Although the high-solids varnish has to release less solvent than the conventional varnish, it leads to stickier films due to the lower molecular weight with only a short crosslinking time. This drying delay can be observed throughout the curing process. In particular, when testing the drying degrees under load with 20 N at drying degree 4 and 200 N at drying degree 6, one can notice the strongly delayed drying.

	conventional	High Solid
Dust free	15 min	100 min
Tack free	180 min	240 min
Drying level 4	180 min	480 min
Drying level 6	240 min	> 9 h / < 16 h

Table 2: Drying comparison polyacrylate - conventional vs. high solid

The basic hardness of the coatings is also different. Figure 7 shows the pendulum hardness development in comparison. The initial hardness, but also the final hardness of the high solid coating is noticeably lower than that of the coating based on the conventional binder.

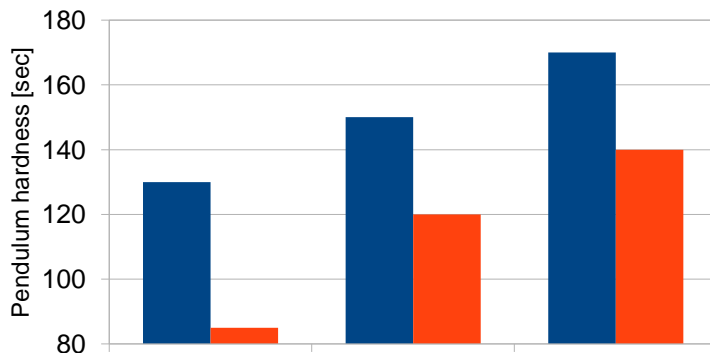


Figure 7: Pendulum hardness polyacrylate - conv. vs. high solid
 ■ conventional ■ High Solid

Especially the drying properties, but also the hardness development can be accelerated by small additions of suitable catalysts. These catalysts accelerate the reaction between the isocyanate and hydroxyl groups. In principle, different products can be used as catalysts. Tertiary amines and metal salts based on tin, zinc and bismuth, for example, are particularly suitable.

Table 3 shows the influence of different catalysts on the drying properties of a high-solids two-component polyurethane coating. Without a catalyst, the coating takes 600 minutes to reach drying level 4. Depending on the catalyst, the time in this case drops to 350 or 230 minutes.

	without	Catalyst A	Catalyst B	Catalyst C
Drying degree 1	30 min	20 min	20 min	20 min
Drying degree 4	600 min	350 min	350 min	230 min

Table 3: Drying - different catalysts in 2 K HS top coat

In addition to accelerating the drying process, the catalysts also increase the hardness of the paint system. Figure 8 clearly shows that the initial hardness of the paint system in particular is noticeably increased after 24 hours. In these cases, the pendulum hardness is up to 50 seconds higher. However, after 48 hours it can already be seen that the pendulum hardness levels off again. After 72 hours, all the coatings are at the

same level. The coating with catalyst C even shows a lower hardness than the non-catalyzed coating.

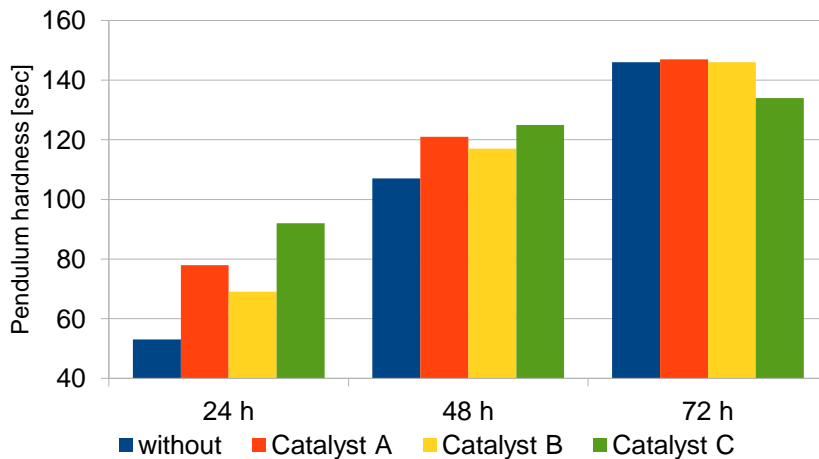


Figure 8: Pendulum hardness of different catalysts in 2 K HS top coats

On the other hand, however, it should not be forgotten that accelerating drying by using suitable catalysts usually also leads to a faster increase in viscosity. Assuming that a doubling of the viscosity means the end of the pot life, the catalyzed coatings cannot be processed as long as the non-catalyzed one. If the non-catalyzed varnish can still be processed well after more than six hours, this can only be guaranteed between two and four hours when catalyst C is used [Tab.4].

	without	Catalyst A	Catalyst B	Catalyst C
Start	24 sec	27 sec	27 sec	26 sec
2 h	30 sec	42 sec	43 sec	43 sec
4 h	35 sec	55 sec	49 sec	57 sec
6 h	40 sec	67 sec	61 sec	69 sec

Table 4: Increase in viscosity - different catalysts in 2 K HS top coats

Limitations in the further development of the systems

In summary, a few things can be stated. In the further development of binders for two-component polyurethane coatings in particular, one comes up against some limits imposed by the technology.

The increase of the non-volatile fraction and thus the reduction of the solvent fraction causes a reduction of the molecular weight with a narrower molar mass distribution. However, this usually also reduces the reactivity of the systems with the same hydroxyl content. A reduction in the solvent requirement is usually not possible with improved drying at the same time.

Suitable catalysts can be used to optimize the drying and crosslinking properties. Due to the type of crosslinking, however, the viscosity increase is also accelerated here, which means a reduced pot life or processing time. Too high reactivities can make the use of so-called two-component spraying systems necessary. Here, components A and

B are mixed in a mixing chamber in front of the spray nozzle directly before application. This increases the effort, especially for the plant technology, and requires the use of highly qualified personnel. For this reason, it is generally attempted to dispense with such processes.

Silane-functional polyurethane-urea binders based on WorléePur Si technology

Products based on the so-called WorléePur Si technology can serve as a basis for optimizing the limitations of classic two-component polyurethane coatings. They are based on available and known technologies and also contain urethane groups, so they are related to the classic polyurethanes .

Chemical structure

The products of the WorléePur Si range are based on a variety of chemical components and contain different essential property groups.

Figure 9 shows the chemical structure. The products based on this technology

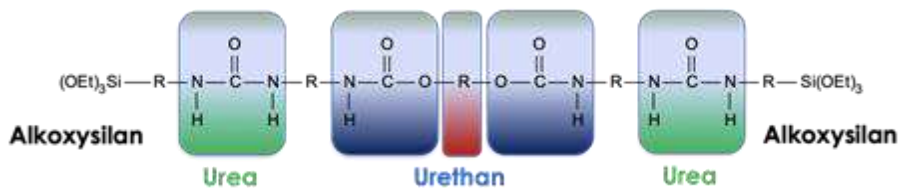


Figure 9: Chemical structure of WorléePur Si technology

are silane-functional polyurethane-urea binders and are also block copolymers with hard and soft segments and inorganic-organic hybrid binders.

The products are manufactured in various steps. The basis for the technology is a polyol. This basic body usually represents the soft segment. It essentially influences the flexibility, hydrolysis and light resistance. In principle, a large number of polyols are possible, which can be used alone or in combination. Polyols such as alkyd resins, polyesters, polycarbonate diols, polyethers or even polyacrylates are possible. These base products usually have to be specially developed and adapted for the subsequent manufacturing process.

The polyols are selected according to the intended use. Alkyd resin-based products are suitable for use in paints, glazes or floor oils, for example. Here, the products ensure a more comfortable processing by brush and roller. These products are also more compatible with known solvents such as de-aromatized hydrocarbons or glycol ethers.

Polyethers are suitable as base polyols in fast-drying systems for interior applications, primers or to achieve special haptic effects. They can be formulated in a wide variety of ways and enable a wide range of properties, such as extremely hard or extremely soft end products. On the other hand, their weather or light resistance is not optimal.

If you need durable and high-quality products for outdoor applications, for example, polyester or polycarbonate diols are suitable as the base polyol. Both technologies also allow a wide range of variations to the conditions.

To further optimize the properties, it may be necessary to use a combination of different polyols, which is usually not a technical problem.

In the first reaction step of the technology, the polyols are reacted with an isocyanate monomer. Due to the later expected properties in terms of yellowing and outdoor resistance, aliphatic isocyanate monomers such as isophorone diisocyanate (IPDI) or trimethylhexamethylene diisocyanate (TMDI) are usually used. When used in excess, these result in an isocyanate-containing prepolymer.

During this reaction, the urethane group is formed, which is one of the hard segments contained. Thus, it provides good tensile strength, toughness, hardness and abrasion resistance.

The isocyanate-containing prepolymer mentioned above is reacted with an aminosilane in a further reaction step. Here the urea group is formed and at the same time an alkoxy silane group is introduced into the polymer.

The urea group is also one of the hard segments mentioned. Compared to urethane groups, this group rather provides for an improvement of the hardness and additionally an optimized scratch resistance. Properties such as tensile strength or tough elasticity are not optimized by this group.

The introduced alkoxy silane group is responsible for the subsequent chemical crosslinking of the WorléePur Si technology products. In addition, it carries the inorganic component silicon. The group therefore additionally ensures further improved scratch resistance, hydrophobicity and improved thermal stability.

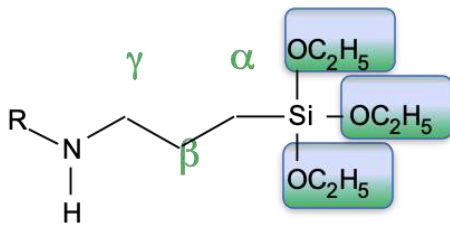


Figure 10: γ - Silane terminated

The products presented are γ -silane-terminated binders [Fig. 10]. Compared to α -silane-terminated products [Fig. 11], these show higher flexibility, improved hydrophobicity and thermal stability. However, chemical crosslinking also takes place more slowly.

In addition, they are ethoxysilanes, i.e. they split ethanol during chemical cross-linking.

Compared to methoxysilanes, which split methanol during crosslinking, this ensures significantly improved storage stability of the products, but also slower drying. However, the methanol alone as a blocking group of the methoxysilanes can lead to difficulties due to the labeling.

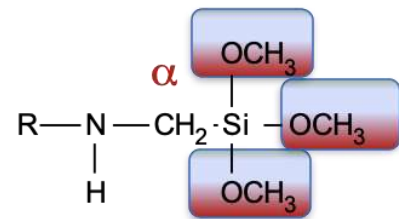


Figure 11: α silane terminated

Networking and catalysis

The crosslinking of the silane-functional polyurethane-urea binders takes place, as with other silane-functional systems, in two phases corresponding to the sol/gel process. The two phases are, on the one hand, hydrolysis [Fig. 12], for which water is required, for example from the air. Here, the blocking agent releases ethanol and a silanol group is formed. This is an equilibrium reaction, the split-off alcohol must be removed so that the hydrolysis can take place to a sufficient extent. The second phase is the polycondensation, i.e. the actual cross-linking of the molecules. This phase can be divided into two different steps, which are important for drying in coatings. As long as

the water content is sufficiently high, a sufficient number of silanol groups can form [Fig. 13], each of which can then crosslink directly with another silanol group, forming a siloxane with the elimination of water. This reaction essentially takes place where the water content is greatest, i.e. on the applied coating surface. As soon as the lacquer surface is sufficiently dry, there may no longer be sufficient water available for complete hydrolysis of the silane groups. If condensation can only take place with sufficient water



Figure 12: Hydrolysis of the ethoxysilane groups

and therefore sufficient silanol groups, then crosslinking would now stop and the varnish would not be able to dry to usual or high film thicknesses. However, polymers can also crosslink if not enough silanol groups are available. In this case, silanol groups formed can crosslink directly with an ethoxysilane group, splitting off ethanol to form a siloxane [Fig. 14]. This condensation step ensures that the applied coatings dry well in thicker layers.

Basically, the binders based on WorléePur Si technology are relatively inert, which is particularly important for storage stability. For the chemical crosslinking, however, a catalyst is required that catalyzes both the hydrolysis and the

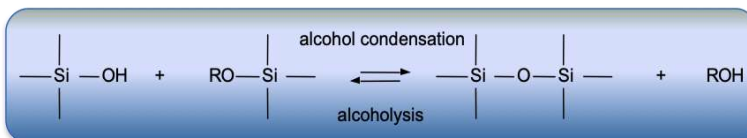


Figure 14: Condensation with excess alcohol

condensation and thus enables them to take place sufficiently quickly. Acid catalysts have proven to be very suitable for this purpose in many tests. Basically, para-toluenesulfonic acid, dodecylbenzenesulfonic acid or alkyl phosphates are well-known acids in the coatings sector.

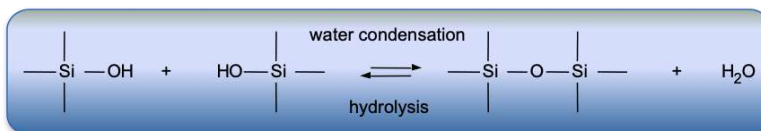


Figure 13: Condensation with excess water

Therefore, depending on the selected coating formulation, it is necessary to achieve a good balance between chemical crosslinking and pot life or processing time. Here, special alkyl phosphates [Fig. 15] in particular have achieved very good results.

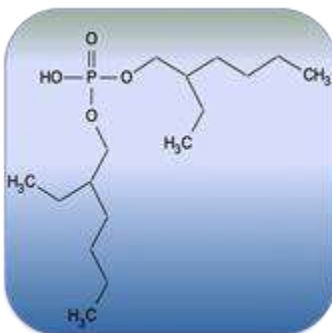


Figure 15: Special alkyl phosphate

superstructure formation

Polyurethanes and polyureas tend to undergo pronounced phase separation [Fig. 16] during film formation. Crystalline / hard areas are formed in a crystalline matrix. This phase separation takes place through the formation of hydrogen bonds between individual polymer chains. Urethanes can form monodentate hydrogen bonds. Ureas have the ability to form both monodentate and bidentate hydrogen bonds.

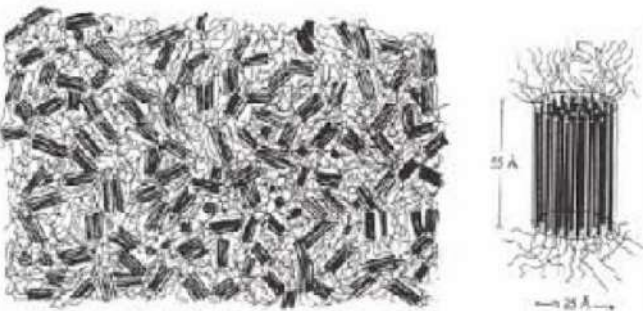


Figure 16: Illustration of phase separation

The products based on WorléePur Si technology contain both two urethane and two urea groups per molecule. Therefore, these products tend to a very strong phase separation. This strong formation of hydrogen bonds corresponds to a type of physical pre-crosslinking. Binders with higher melting ranges, improved tensile strength and better durability are obtained.

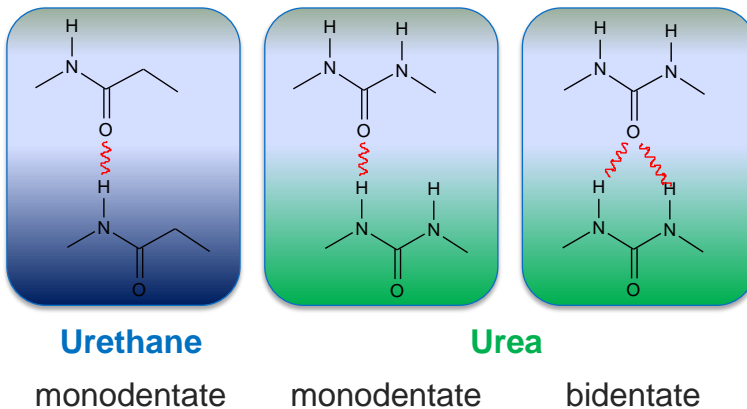


Figure 17: Formation of hydrogen bonds

Properties compared to classic two-component polyurethane coatings

The silane-functional polyurethane-urea binders of the WorléePur Si series are also polyurethanes, but still modified polyurethanes. Where classic two-component polyurethane coatings reach their limits, these allow further optimization of certain important properties in high-quality coating systems.

Pot life and processing time

An important property of two-component coatings is the pot life or processing time. It indicates how long a coating can be processed after the reaction components have been mixed or activated by a catalyst, for example. The pot life is often given as the time it takes for the coating to double its viscosity. The processing time describes something different. This tends to look at how long it takes to achieve certain and important properties. For example, the rheological properties of a coating change with increasing viscosity, which can lead to poorer flow or even surface defects. This processing time can possibly be reached after an increase in viscosity of perhaps ten seconds. However, this is essentially dependent on the application. Clear or top coats are certainly more critical than primers, since they do not always have to achieve perfect flow. Working times that are too short require the coating to be applied quickly and allow only a few corrections during application. If these are particularly short, for example much less than 30 minutes, it may even be necessary for the paint to be processed using a so-called two-component spraying system. In this case, the basecoat and the hardener are only mixed directly in front of the spray nozzle. In this case, the rapid increase in viscosity no longer plays a role. However, this type of application is more time-consuming and is often avoided if possible.

The use of silane-functional polyurethane-urea binders usually allows significantly longer pot life and processing times compared to classic two-component polyurethane coatings.

In Table 5, one can see quite clearly the differences in the viscosity increase of two high solid topcoats. The high solids two-component polyurethane coating needs slightly more than two hours to double its viscosity. On the other hand, the high-solids coating based on WorléePur Si technology needs between 48 hours and one week for this.

In comparison, the paint activated in this way can also be processed for more than 48 hours. This means that paint residues no longer have to be disposed of. On the other hand, waiting times between, for example, a second spray application or a longer break are no longer a problem. Cleaning of the spraying equipment can also be postponed if necessary.

	2 K PU HS top coat	WorléePur Si HS Topcoat
Start	21 sec	19 sec
2 h	39 sec	23 sec
4 h	48 sec	24 sec
6 h	58 sec	24 sec
24 h	-	26 sec
48 h	-	34 sec
1 week	-	48 sec

Table 5: Viscosity increase of top coats 2 K PU HS vs. WorléePur Si HS

In the formulation of clear coats, these potting or processing times can be even significantly longer. Table 6 shows the comparison of the viscosity increase of two furniture lacquers. Even the classic two-component polyurethane varnish based on a conventional acrylate has a pot life of about 24 hours. The lacquer based on the WorléePur Si technology can even be processed after more than two weeks after

activation. In most cases, such a long processing time may not be necessary, but it shows the possibilities of the technology.

	2 K PU clear lacquer	WorléePur Si Clear Lacquer
Start	21 sec	21 sec
2 h	26 sec	23 sec
4 h	30 sec	23 sec
6 h	32 sec	23 sec
24 h	42 sec	24 sec
48 h	-	25 sec
1 week	-	29 sec
2 weeks	-	31 sec

Table 6: Viscosity increase of silk gloss furniture lacquers 2 K PU vs. WorléePur Si

The reasons for the longer processing times are the absence of pigments and fillers, some of which introduce certain amounts of water into the system and thus enable or support hydrolysis in the container.

Differences and explanation

An explanation for the very different pot life and processing times can be found when looking at the different types of crosslinking. The crosslinking of the classic two-component polyurethane coatings takes place between the hydroxyl groups of the polyols and the isocyanate groups of the hardener. This is an addition reaction [Fig. 18].

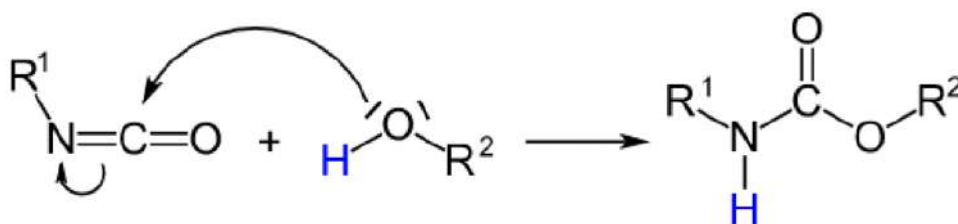


Figure 18: Addition reaction between isocyanate and hydroxyl group

This starts directly after the mixing of the components, takes place in the whole container and usually cannot be stopped. Also, no split products are formed that have to be removed.

The silane-functional polyurethane-urea binders must hydrolyze before actual crosslinking [Fig. 19].

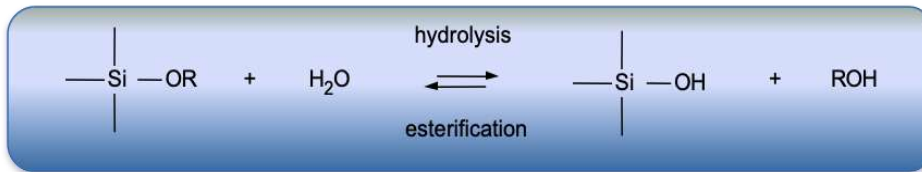


Figure 19: Hydrolysis of silane-functional polyurethane-urea binders

In this process, water is absorbed and the blocking agent ethanol is split off. This reaction takes place in equilibrium, so if water is to be absorbed, then ethanol must also be removed. The essential water absorption and thus also hydrolysis takes place on the surface of the paint in the can and not in the whole container, because the water cannot reach there well. On the other hand, the solvent used (partly alcohols) and the ethanol released form a saturated solvent atmosphere in the container, which ensures that not much water can reach the coating.

Storage of already activated coatings

Even with already activated coatings one can take advantage of the fact that hydrolysis is an equilibrium reaction. Even after adding the catalyst, the pot life or processing time can be drastically extended or even partially prevented. For this purpose it is necessary that the containers are well closed. If the ethanol that may have formed is not removed, then the hydrolysis stops. The proportionate use of an alcohol is also helpful. This ensures a saturated atmosphere in the closed can, which can also reduce hydrolysis. Table 7 shows the viscosity increase of activated stored varnishes after different storage times at 50°C, which were opened for application. These were compared with a freshly prepared varnish. During storage, a certain increase of the initial viscosity is observed compared to the freshly activated varnish. However, the subsequent increase in viscosity after opening the containers takes place at a comparable level. The initial viscosity, even after storage, can certainly be brought to the value required for processing by optimizing the coating formulation.

	Fresh paint	6 weeks storage at 50°C	12 weeks storage at 50°C
Start	48 sec	54 sec	60 sec
2 h	50 sec	56 sec	61 sec
4 h	50 sec	56 sec	61 sec
6 h	52 sec	58 sec	63 sec
24 h	53 sec	57 sec	63 sec
48 h	59 sec	59 sec	64 sec
1 week	60 sec	59 sec	68 sec
2 weeks	64 sec	66 sec	73 sec

Table 7: Processing time top coat after storage at 50°C

To a very small extent, the initial viscosity increases during storage of the activated coatings. So it may well be that other properties are also affected.

Over twelve weeks of storage at room temperature, the activated coating shows no worsening of the drying properties [Tab. 8]. With a comparable storage time, but at 50°C, a longer time to reach drying level 6 is observed.

	Fresh paint	12 weeks storage at r.t.	12 weeks storage at 50°C
dust-dry	10 min	10 min	10 min
non-tacky	40 min	30 min	30 min
Drying level 4	1 h	1 h	1 h
Drying level 6	2 h	2 h	3 h

Table 8: Change in drying time during storage

The pendulum hardness development after storage at room temperature and 50°C also shows a different picture [Tab. 9]. The paint stored at room temperature showed a comparable hardness development even after the twelve weeks of storage. After this storage time, storage at 50°C leads to a noticeable reduction of the hardness development with only slightly reduced final hardness.

	Fresh paint	12 weeks storage at r.t.	12 weeks storage at 50°C
2 h	28“29“	29“29“	26“26“
24 h	138“138“	146“142“	102“102“
48 h	164“161“	154“153“	129“128“
1 week	178“176“	185“182“	168“161“

Table 9: Change in hardness development during storage

Nevertheless, already activated varnish can be stored for a very long time. After twelve weeks at room temperature, one can hardly notice any differences to a freshly produced varnish. Even when stored at 50°C, you still get a fast drying and high quality lacquer after twelve weeks of storage. Certainly, the possible storage time of activated coatings will depend on the selected coating formulation. Highly filled coatings contain more fillers which may contain water. It can therefore be assumed that the possible storage time is reduced here. Clear lacquers, on the other hand, contain few water-bearing components. Therefore, a longer possible storage time can be expected here.

Drying and cross-linking

Sufficiently fast drying and cross-linking of the paint film after application is important for further handling of the painted objects. For industrial coatings, fast drying is desirable in most cases, since the application is usually carried out by spraying and thus a longer open time is not necessary.

Basically, you can measure the drying time in different ways. The determination of dust-dry and tack-free is rather subjective. The dust-dry condition indicates when no visible trace can be seen when lightly stroking the paint surface with a finger. This test can be compared with dryness level 1. In this case, small glass beads scattered on the surface

can be easily and completely removed with a hair brush. Stick-free, on the other hand, indicates when the coating film no longer sticks when light pressure is applied by the finger. If we take the measurement of degrees of dryness as a basis here as well, we can compare this condition with degree of dryness 3. Here, paper weighing 200 grams is placed on the coating surface. After one minute of testing, the paper should no longer stick. However, it is much more interesting to see how long it takes for the coating to be able to withstand higher pressures. Important measurements in this respect are the drying degrees 4 and 6. To determine drying degree 4, a piece of paper is placed on the coating surface with a load of two kilograms and for drying degree 6 with 20 kilograms for one minute. In both cases, the paper must not stick after the load. A slightly visible change in the coating surface, on the other hand, is permissible. ⁱ

In Table 10, the possibilities of the silane-functional polyurethane-urea technology in comparison to conventional two-component polyurethane coatings can be seen well. Both coatings show similar test viscosities and non-volatile contents in this test. In comparison, the paint based on WorléePur Si technology dries drastically faster. Dryness level 4 is reached after just 50 minutes and dryness level 7 after 75 minutes. The classic coating requires 960 and 1200 minutes respectively.

	2 K HS PU top coat	WorléePur Si HS Topcoat
dust-dry	180 min	15 min
non-tacky	480 min	45 min
Drying level 4	960 min	60 min
Drying level 6	1200 min	75 min

Table 10: Drying comparison 2 K HS PU vs. WorléePur Si HS

The pendulum hardness, on the other hand, is definitely a measure of the progressive cross-linking of the paint film. For this purpose, a pendulum with two balls periodically swings over the dried paint surface. In the process, the balls penetrate the paint surface in accordance with the plastic-elastic behaviour and the pendulum is damped to a greater or lesser extent. The time in seconds required to fall between a specific pendulum range is measured. Hard and less elastic films achieve higher pendulum hardnesses than soft and elastic films ⁱⁱ. This measurement method is not optimal in every case, as resilient films, for example, can achieve lower pendulum hardnesses simply because they are more flexible. However, when testing similar coating systems, the values are suitable for comparison. And here the initial pendulum hardnesses compared to the final hardnesses can give a good indication of the crosslinking speed. Similar to the observation of the drying speed, the coatings show great differences in their behaviour with regard to hardness development [Tab 11]. After sufficient curing time, both coatings reach a very similar hardness. The differences are more apparent after shorter test times. Already after two hours drying time the WorléePur Si coating reaches the same hardness as the two component polyurethane coating after 24 hours. And here the WorléePur Si lacquer has already reached more than 80% of its final hardness.

	2 K HS PU top coat	WorléePur Si HS Topcoat
2 h	-	42 sec
24 h	46 sec	150 sec
48 h	114 sec	160 sec
72 h	150 sec	170 sec
1 week	168 sec	177 sec
2 weeks	165 sec	178 sec

Table 11: Comparison of hardness development 2 K HS PU vs. WorléePur Si HS

But even if conventional, i.e. not high-solids, coatings based on silane-functional polyurethane-urea binders dry faster than classic two-component polyurethane coatings.

The coatings compared in Table 12 contain significantly higher proportions of solvents. The OH functional polyacrylate used in the 2 K PU clearcoat has a significantly increased molecular weight. These advantages over the high solid varnish are also reflected in the drying times of the various tests. Nevertheless, the coating based on WorléePur Si technology still dries much faster than the comparative coating. Dryness level 6 is reached after a good half of the time.

	2 K PU clear lacquer	WorléePur Si Clear Lacquer
Dust free	15 min	10 min
Tack free	180 min	60 min
Drying level 4	180 min	60 min
Drying level 6	240 min	120 min

Table 12: Drying comparison 2 K PU clearcoat vs. WorléePur Si clearcoat

As in the comparison of the high solid coatings, the clearcoat based on the silane-functional polyurethane-urea binder allows an earlier measurement of the pendulum hardness [Tab. 13]. After only two hours, a dry film is obtained which allows a measurement. After at least six hours, the hardness of the two-component polyurethane coating can also be measured. Here, the pendulum hardness is less than half that of the coating based on the silane-functional polyurethane-urea binder.

After about 24 hours, however, the hardnesses equalize and a comparable hardness development can be observed. Here, too, a significantly faster crosslinking can be observed when using the WorléePur Si technology.

	2 K PU clear lacquer	WorléePur Si Clear Lacquer
2 h	-	42 sec
6 h	35 sec	82 sec
24 h	130 sec	113 sec
48 h	150 sec	148 sec
1 week	170 sec	175 sec

Table 13: Comparison hardness development 2 K PU clearcoat vs. WorléePur Si clearcoat

Another and perhaps better test to determine the fast and good cross-linking is the test of MEK resistance. MEK, methyl ethyl ketone or butanone is an organic solvent with very good dissolving power. In this test, a piece of cotton wool soaked in MEK is moved in strokes over the dried paint surface. Here, the double strokes are counted until the paint surface is damaged. The maximum value is 200 double strokes. At this value, a very good resistance can be assumed. Depending on the drying time, this MEK resistance gives a good possibility to observe the progress of the chemical crosslinking.

Classic two-component polyurethane coatings achieve very good MEK resistance after sufficient crosslinking. However, the comparison in Table 14 clearly shows the differences between the various technologies. Both coatings achieve a MEK resistance of 200 double strokes after one week of drying. However, the coating based on the WorléePur Si binder reaches this value after only six hours of drying. The two-component polyurethane, on the other hand, achieves four double strokes after this time.

	2 K PU furniture lacquer	WorléePur Si Furniture Varnish
6 h	4	200
24 h	29	200
1 week	200	200

Table 14: Comparison MEK resistance 2 K PU furniture lacquer vs. WorléePur Si furniture lacquer

The various investigations regarding drying and cross-linking clearly show advantages on the side of the WorléePur Si technology.

Differences and explanation

To explain the faster drying and cross-linking, we need to take another look at the differences between the cross-linking technologies.

As already described, the two-component polyurethane coatings crosslink by an addition reaction between hydroxyl and isocyanate group. There may be some side reactions in this process. For example, the isocyanates may also react with amine groups present in the coating system, which may be present in dispersants, for example. On the other hand, it may also react with other hydroxyl group carriers, such as water or solvents.

The silane-functional polyurethane-urea binders, on the other hand, must first hydrolyze and then crosslink by means of polycondensation. No side reactions are known. The comparison of the crosslinking mechanisms does not explain the differences in drying properties and crosslinking.

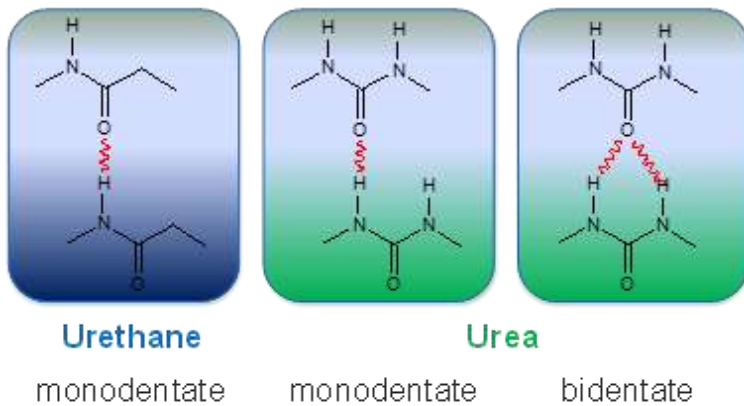


Figure 20: Formation of hydrogen bonds

To do this, we need to take another look at the chemical structure of the different products. As previously described, polyurethane and urethane groups interact relatively strongly with each other via hydrogen bonds. Urethane groups can form monodentate and urea groups can form monodentate and bidentate hydrogen bonds [Fig. 20]. The silane-functional polyurethane-urea binders of the WorléePur Si series have a large

number of these groups. Each individual polymer can interact with another in its vicinity. Since the polymers are optimally arranged in relation to each other and thus the silane groups, which are important for cross-linking, are also optimally arranged in relation to each other, they can react with each other directly after hydrolysis. Alignment via hydrogen bonds can also take place in the classic two-component polyurethane coatings. However, only the isocyanate hardeners interact with each other via this physical bond, since only these contain corresponding urethane groups. Thus, an interaction with the polyols containing hydroxyl groups only takes place via the chemical reaction between hydroxyl and isocyanate groups, which certainly takes longer than in the case of a prior or simultaneous alignment of the polymers for hydrolysis and subsequent polycondensation of the WorléePur Si products. On the other hand, although hydrogen bonds do not represent a strong chemical bond, they do provide some physical pre-crosslinking when the number is high.

Development possibilities, product characteristics and application examples

Development opportunities

The WorléePur Si technology offers many possibilities to develop suitable products for the requirements of the paint manufacturer. The base polyol determines a large part of the properties of the final product and can be selected accordingly. Alkyd resins as

polyol improve the solubility in dearomatized test benzenes, optimize the processing properties with brush and roller and allow alkyd resin like surfaces for example on wood. Polyester or carbonated diol based polyols are more suitable for use in industrial coatings as they provide faster drying, higher hardness, better weather and chemical resistance. Mixtures of different polyols to control the properties are also conceivable. A further adjusting screw is the isocyanate monomer, which is required for the production of the isocyanate-containing prepolymer. Since the products are usually used outdoors and should therefore not yellow too much, aliphatic isocyanate monomers such as isophorone diisocyanate (IPDI) or trimethyl hexamethylene diisocyanate (TMDI) will certainly be used.

There are also few limits in the range of possible solvents. Only for the synthesis and optimal stability of the products, small amounts of alcohols or ethers should be used. Other solvents can be selected according to the solvents normally used in the field of application. For example, dearomatized hydrocarbons with glycol ethers are suitable for paints, glazes and oils. In industrial paints, solvents such as esters (e.g. butyl acetate), aromatic solvents (e.g. xylene) or ketones (e.g. acetone) with proportions of alcohols such as propanol are possible.

For the formulation of very high solids coatings the use of reactive thinners may be necessary. These are low molecular weight ethoxysilanes without further functionalities. For example, products such as tetraethyl orthosilicate (TEOS), isobutyltriethoxysilane (IBTEO) or methyltriethoxysilane (MTES) are used. Selected according to the required drying speed, these products in combination with the binders allow a significant increase in the non-volatile content while maintaining low viscosity.

Nomenclature

In principle, silane-functional polyurethane-urea binders can be used in a wide variety of applications due to their variability.

The nomenclature of the products is essentially based on the name of the product group and the base polyol used, which can be identified by the first figure of the four-digit number. All products are united by the name "WorléePur Si". The "Si" in the name stands for silane modification. The part "Pur" results from the polyurethane contained. The first digit corresponds to the following base polyols:

- 1 = Alkyd resin
- 2 = Polyester polyol
- 3 = polyacrylate
- 4 = polycarbonate diol
- 5 = Polyether polyol

Properties in comparison - WorléePur Si 2021, 2031 and 4011

For industrial applications the three products WorléePur VP Si 2021, WorléePur VP Si 2031 and WorléePur VP Si 4011 can be used. If necessary, variations based on these products or the base polyols used are available. Table 15 gives an overview of the delivery form and the base polyol used. These basically lead to different properties in the products. WorléePur VP Si 2021 was developed on the basis of a specially modified polyester polyol. This is a hard segment modification, which should give the polyol a

faster drying and higher hardness. Also for the development of WorléePur VP Si 2031 a polyester polyol was used. However, this does not have any additional modification. In this case a higher flexibility should be achieved, nevertheless with high hardness and fast drying. For the build-up of WorléePur VP Si 4011 a special carbonate diol was used, which in connection with the WorléePur Si technology should lead to a product with high flexibility and nevertheless good mechanical strength. Due to the very regular structure and thus low branching, it also leads to products with lower viscosity, which allows a higher non-volatile content.

	WorléePur VP Si 2021	WorléePur VP Si 2031	WorléePur VP Si 4011
nvc	75% in butyl acetate / n-propanol	75% in butyl acetate / n-propanol	80% in butyl acetate / n-propanol
Polyol base	Polyester with hard segment	Polyester	Carbonatediol

Table 15: Delivery form and polyol base WorléePur VP Si 2021, 2031 and 4011

Simple top coat formulation

A simple formulation for a topcoat was chosen to compare some properties. A comparable formulation was used for all products. Table 16 shows the composition of the coating recipes used for the comparison. It is easy to see that the usual raw materials were used. With the pigments and fillers, there is no need to look for water-free qualities, since the water contained is well bound. It is also not absolutely necessary to use water-free versions of solvents. At most, relatively pure qualities should be used for alcohols. For example, technical ethanol contains up to 7% water, which after the addition of the catalyst can lead to a reaction that is clearly too fast and thus to a short pot life or processing time.

The WorléePur Si products are block copolymers with hard and soft segments. Due to this structure they already wet pigments and fillers very well. For further support, dispersants such as WorléeDisperse 8110 S are suitable. When using dispersants, pH neutral types with only small amounts of amine groups should rather be used. Since the catalyst is an acid, these groups can react with the acid groups and deactivate it. This can lead to a slow or incomplete reaction during the drying process. If it is not possible to do without such dispersants, then the amount of catalyst must be increased accordingly.

For the thinning of the lacquers based on WorléePur Si technology, a variety of solvents are suitable. In this case, butyl acetate is the essential solvent. To optimize the dilution, ethanol and methoxypropanol were also used. Alcohols and ethers improve solubility and lower viscosity more than aromatic solvents, ketones or esters. Their different evaporation rates also make it possible to optimize the drying, through-drying, flow and also the open time.

Recipe	WorléePur VP Si 2021	WorléePur VP Si 2031	WorléePur VP Si 4011
WorléePur VP Si 2021 75% BAC / n-propanol	55,30		
WorléePur VP Si 2031 75% BAC / n-propanol		55,30	
WorléePur VP Si 4011 75% BAC / n-propanol			51,85
WorléeDisperse 8110 S	0,50	0,50	0,50
WorléeAdd 820 Paste, 10% in Xylene	3,00	3,00	3,00
Kronos 2360	14,08	14,08	14,08
Hostapermblue B2G-L	0,18	0,18	0,18
Bayferrox 3920	0,55	0,55	0,55
Printex 200	0,06	0,06	0,06
Blanc fixe micro	7,50	7,50	7,50
HansaAdd 4090	0,05	0,05	0,05
Butyl acetate	13,78	13,78	17,23
Ethanol	2,00	2,00	2,00
Methoxypropanol	3,00	3,00	3,00

Table 16: Masterbatches WorléePur Si 2021, 2031 and 4011

Technical data of the ready-to-use coatings

Before testing the paints, the base paints were mixed with the catalyst and adjusted for processing time. As seen in Table 17, the addition of the catalyst is very small. For a more convenient mixing ratio, the catalyst can also be diluted with solvent. The added solvent should then be left out of the coating recipe accordingly.

The catalyst-activated coatings were adjusted with a mixture of butyl acetate and n-propanol in a 1:1 ratio to a viscosity between 30 and 50 seconds run-out time in a 4 mm run-out cup. The varnish based on WorléePur VP Si 4011 was already very low viscous without additional solvent. The largest addition of solvent was needed for the WorléePur VP Si 2031 based coating. Also for the adjustment of the WorléePur VP Si 2021 based coating, solvent had to be added, but significantly less.

After adjusting the coatings, the non-volatile content and the density were determined and the VOC content was calculated. Here, of course, the previous different solvent

additions are noticeable. The WorléePur VP Si 4011 leads to the highest non-volatile content and accordingly to the lowest VOC. The lowest non-volatile content in this comparison is achieved by WorléePur VP Si 2031, because here also the highest amount of solvent was needed to adjust the viscosity. WorléePur VP Si 2021 lies between the two products.

Recipe	Si 2021	Si 2031	Si 4011
Base paint WorléePur VP Si 2021	100,00		
Base paint WorléePur VP Si 2031		100,00	
Base paint WorléePur VP Si 4011			100,00
Catalyst WorléeAdd 2100	1,00	1,00	1,00
Adjust viscosity DIN 4/20°C to 30-50 sec with BAC/n-propanol 1:1	78 sec + 5 g solvent	172 sec + 14 g solvent	
	46 sec	49 sec	36 sec
nvc	58,70%	54,10%	61,40%
Density, 20°C g/cm ³	1,17 g/cm ³	1,14 g/cm ³	1,17 g/cm ³
VOC content	483 g/l	523 g/l	452 g/l

Table 17: Technical data ready-to-use coatings

Pot life or processing time

Even though the pot life of the products based on WorléePur Si technology is significantly longer than that of classic two-component polyurethane coatings, they still differ from each other.

In the non-optimised formulation chosen here, WorléePur VP Si achieves a pot life of about 24, WorléePur VP Si 2031 of more than 6 hours and WorléePur VP Si 4011 of about one week.

Recipe	WorléePur VP Si 2021	WorléePur VP Si 2031	WorléePur VP Si 4011
Pot life			
Start	46 sec	49 sec	36 sec
2 h	56 sec	69 sec	41 sec
6 h	72 sec	82 sec	45 sec
24 h	90 sec	120 sec	55 sec
48 h	177 sec	245 sec	64 sec
1 week	solid	solid	73 sec

Table 18: Pot life / processing time

Drying properties and hardness development

The comparison of the drying properties, the hardness development and thus also the crosslinking progress was carried out by means of various tests [Tab. 19].

All coatings were applied to glass with a wet film thickness of 100 µm. After complete drying, this corresponds to a dry film thickness of about 40 µm.

First, the drying modes dust-dry and tack-free were determined. The coatings based on the products WorléePur VP Si 2021 and 2031 achieve almost comparable drying times, of seven and eight minutes for dust drying and around 70 minutes for a tack-free film. Whereby it should not be forgotten that the WorléePur VP Si 2021 leads to a more than 4% higher non-volatile content. The coating based on WorléePur VP Si 4011 needs significantly longer for both drying processes with more than 20 and 160 minutes respectively.

After two, three and six hours respectively, the drying stage 4 and 6 were determined. The differences between the individual products can be seen particularly clearly in this load test. After only two hours the coating based on WorléePur VP Si 2021 reaches drying stage 6, whereas the coating based on WorléePur VP Si 2031 needs three hours and the coating based on WorléePur VP Si 4011 six hours.

The differences and the effect of the base polyols can also be clearly seen when looking at the development of the pendulum hardness. With the products WorléePur VP Si 2021 and 2031 a comparable pendulum hardness can already be measured after two hours. The varnish based on WorléePur VP Si 4011 is still too soft and sticky here. After six hours drying time already bigger differences can be observed. Here the WorléePur VP Si 2021 already leads to a higher pendulum hardness than the 2031 and 4011. This increases during the drying process. Even after one week of drying, a large difference in pendulum hardness can be observed.

Recipe	WorléePur VP Si 2021	WorléePur VP Si 2031	WorléePur VP Si 4011
100 µm wet film corresponds to approx. 40 µm DFT			
Dust free	7 min	8 min	23 min
Tack free	76 min	70 min	162 min
Drying stage after 2 h	6	4	4
Drying stage after 3 h	6	6	4
Drying stage after 6 h	6	6	6
Pendulum hardness			
2 h r.t.	26°26°	25°25°	-
6 h r.t.	67°68°	61°60°	38°39°
24 h r.t.	126°125°	107°106°	71°72°
48 h r.t.	142°140°	125°127°	81°82°
72 h r.t.	147°148°	125°124°	84°84°
1 week r.t.	168°168°	136°136°	93°95°

Table 19: Drying properties and hardness development

Some mechanical properties

To test some mechanical properties, the coatings based on the different binders were applied to structured cold-rolled steel with a wet film thickness of 120 µm, which corresponds to a dry film thickness of about 50 µm. After 24 hours and two weeks, the Erichsen cupping, the impact (reverse and direct) and the scratch hardness were determined [Tab. 20].

With regard to the Erichsen cupping and the impact test, there are definitely advantages in the selection of the base polyols. The polycarbonate diol in WorléePur VP Si 4011 leads to a very high elasticity in both tests. On the opposite side is the WorléePur VP Si 2021, which leads to noticeably less elastic films. The results of WorléePur VP Si 2031 are about in the middle of both products in the Erichsen cupping, with a very good impact test at the same time.

When testing the scratch hardness, the advantage of the hard segment modification of WorléePur VP Si 2021 is again evident. It allows the highest scratch hardness here, followed by WorléePur VP Si 2031 and 4011.

Recipe	WorléePur VP Si 2021	WorléePur VP Si 2031	WorléePur VP Si 4011
120 µm wet film on grained steel corresponds to approx. 50 µm DFT			
Erichsen depression			
24 h	8.3 mm	8.7 mm	9.4 mm
2 weeks	6.6 mm	8.0 mm	9.3 mm
Impactdirect , 1kg			
24 h	> 100 cm	> 100 cm	> 100 cm
2 weeks	80 cm	> 100 cm	> 100 cm
Impact reverse, 1 kg			
24 h	> 100 cm	> 100 cm	> 100 cm
2 weeks	< 10 cm	90 cm	> 100 cm
scratch hardness			
24 h	1,5 N	1,3 N	0,8 N
2 weeks	2,0 N	1,5 N	1,0 N

Table 20: Mechanical properties

Resistance QUV Rapid weathering

In the selected formulations, the binders allow the formulation of glossy coatings. Table 21 gives an overview of the gloss and shade stability of the coatings in a QUV rapid weathering test. A test consisting of a UV phase at 60°C with an average irradiance of 0.89 W/m² at a wavelength of 340 nm for eight hours was selected here. This wavelength corresponds to UV A radiation. Alternating with the UV phase, a condensation phase runs for four hours. In this phase, the painted sheet is placed in the test chamber without light at 45°C and is exposed to condensing moisture. This quick test allows the observation of the behaviour of the lacquers in relation to solar radiation, as well as rain and thaw. The test allows the observation of a drastically accelerated ageing.

Even without appropriate modification with light stabilizers, the coatings show good gloss and especially shade stability. The WorléePur VP Si 2021 shows slight advantages over the other binders in terms of resistance. The other two products show quite similar behavior.

Recipe	WorléePur VP Si 2021	WorléePur VP Si 2031	WorléePur VP Si 4011
Gloss 60° / Δ E Hue difference			
Start	85	82	86
170 h	82 / 0,05	79 / 0,20	84 / 0,05
500 h	79 / 0,07	74 / 0,22	81 / 0,08
840 h	74 / 0,05	67 / 0,20	72 / 0,18
1000 h	70 / 0,09	62 / 0,35	66 / 0,26
1340 h	64 / 0,22	54 / 0,54	53 / 0,49
1670 h	54 / 0,39	48 / 0,67	45 / 0,65
2000 h	47 / 0,56	42 / 0,81	40 / 0,78

Table 21: QUV A 340 rapid weathering - gloss and shade stability

Outlook

The previous tests only give a small overview of the properties and differences of some products based on WorléePur Si technology. In accordance with the requirements for the surface properties to be achieved, the coatings can be formulated accordingly. The binder plays an important role, but the properties can be specifically influenced by pigments, fillers, additives, solvents or even reactive diluents. In addition to numerous guideline formulations to assist with formulation, the technical experts can also be consulted here.

i <https://www.erichsen.de/de-de/produkte/oberflaechenpruefung/kornfeinheit-deckvermogen-trocknung/trocknung/trocknung/trockengrad-pruefgerat-modell-415/tbd-415.pdf>

ii https://www.r-g.de/wiki/Verarbeitungshinweise:Ma%C3%9Ffeinheiten_und_Pr%C3%BCfverfahren